

Surface Composition and Texture of Titanium Polished with Colloidal Silica Suspension and Chromic Oxide Slurry

Awlad HOSSAIN, Seigo OKAWA and Osamu MIYAKAWA

Division of Biomaterial Science, Course for Oral Life Science, Niigata University Graduate School of Medical and Dental Sciences, Gakkocho-dori 2-5274, Niigata 951-8514, Japan

Corresponding author, E-mail: sokawa@dent.niigata-u.ac.jp

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CP titanium was polished with a colloidal silica suspension and chromic oxide slurry under low and high pressures. The polished surfaces were characterized by means of EPMA and XPS. Irrespective of polishing pressure, colloidal silica suspension successfully created a mirror-like surface that was clean at EPMA level. However, XPS detected a small amount of silicon on the outermost surface. On the other hand, chromic oxide slurry under high pressure yielded a very uneven surface with numerous scratches. The EPMA and XPS results suggested the presence of chromium-containing species in the polished surface, which might include hydroxides as well as oxides. In addition, the level of oxygen concentration was noticeably raised, which probably resulted from the increase of surface oxide film thickness or the extension of oxide-to-metal transition zone.

Key words: Titanium, Polishing, Surface

INTRODUCTION

Titanium has been used for various dental prostheses because of its excellent corrosion resistance and biocompatibility. For its more extensive applications, attention has been paid to various problems: improvement of corrosion resistance by alloying^{1,2)}; development of new investment materials^{3–6)} and clarification of molten titanium flow^{7–9)} for complete castings; laser welding technique for extended prostheses^{10,11)}; and surface modification for high bonding strength to resin^{12,13)}.

However, since titanium has low thermal conductivity, heat that is generated due to interactions with cutting tool does not dissipate quickly, which allows the temperature at cutting point to rise high. Under such conditions, the tool is prone to react with inherently reactive titanium, thus undergoing severe chemical wear. Due to the chemical wear of tool, the machinability and grindability of titanium and its alloys pose a challenge^{14–16)}. These processing difficulties have greatly limited titanium's applications in clinical practice¹⁷⁾. To overcome this problem, some machinable titanium alloys have been developed in the dental field^{18–21)}.

Similarly, titanium is not easy to mirror-finish. A series of studies have focused on the finishing of titanium surfaces^{22–26)}. When abraded or polished with abrasive materials such as silicon carbide²²⁾, aluminum oxide²⁴⁾, or ferric oxide²⁵⁾, the surface composition was substantially altered due to contamination by constituent elements from abrasives. A previous study²⁶⁾ has demonstrated that electrochemical buffing of titanium with α -Al₂O₃ slurry produced a substantially even and chemically clean surface, whereas

mechanical buffing alone resulted in a relatively rough surface containing a substantial amount of aluminum.

Since early times, chromic oxide polishing material has been used for the surface finishing of dental restorations. Recently, colloidal silica suspension has likewise been applied as a polishing agent to titanium surfaces. Thus, it is necessary to investigate whether these polishing materials successfully create a mirror-like surface and if they inadvertently alter the surface composition.

The aim of the present study was to investigate the surface composition and texture of titanium polished with colloidal silica suspension and chromic oxide slurry. For this purpose, all polished surfaces were characterized by means of electron probe microanalysis (EPMA) and X-ray photoelectron spectroscopy (XPS).

MATERIALS AND METHODS

Preparation of specimens

Specimens for EPMA were as-received CP titanium ingots (16 mm in height × 16 mm in diameter) of JIS Class 2 (T-Alloy M, GC, Tokyo, Japan). The specimens were mechanically abraded with water-proof silicon carbide abrasive papers up to #600 grit under tap water cooling.

Specimens for XPS were cast plates of 13 mm in width, 40 mm in length, and 1.4 mm in thickness. CP titanium of JIS Class 2 (Dental Titanium, Ohara, Osaka, Japan) was cast into room temperature mold made from a phosphate-bonded investment material (Titavest II, Ohara, Osaka, Japan). Both sides of cast plates were abraded, as explained in the forego-

Table 1 Polishing agents and buffing cloths used in the present study

	Polishing agent			Buffing cloth	Manufacturer
	Product code	Particle size	pH		
Colloidal silica suspension	OP-S	0.04 μm	9.8	OP-NaP	Struers A/S, Copenhagen, Denmark
Chromic oxide slurry	Metpolish No. 2	0.5 μm	—	Mastertex	Buehler, Lake Bluff, IL, USA

ing paragraph. Finally, the plate thickness was reduced to approximately 0.7 mm. Hence, the abrading process completely removed any surface reaction layer²⁷⁾ that had been formed through reactions of titanium with investment material components.

Using either a colloidal silica suspension or chromic oxide slurry, the abraded specimens were polished under either low (0.05 kg/cm²) or high (5 kg/cm²) pressure. Polishing times were 90 and 20 minutes for low and high pressures respectively. The polishing agents and corresponding buffing cloths used in this study are listed in Table 1. Both abrading and polishing were conducted on a polishing machine (AUTOMAX, Refine Tech, Yokohama, Japan), where the rotational speeds of the buffing cloth and specimen were 130 and 50 rpm respectively. Finally, the specimens were ultrasonically cleaned in acetone.

EPMA

An electron probe microanalyzer (EPMA-8705-III, Shimadzu, Kyoto, Japan) was used to analyze elements present in the polished surfaces. Analysis was done in stage scan mode under the following conditions: accelerating voltage = 15 kV, specimen current = 0.5 μA , scanning step size = 1 μm , and sampling time = 70 ms/step. Lithium fluoride crystal was used to detect Si K α and Cr K α . O K α was detected by using an artificially prepared spectroscopic crystal (LSA, Shimadzu, Kyoto, Japan), which is 10 times or more as sensitive as a spectroscopic crystal of rubidium acid phthalate. Secondary electron (SE) im-

ages were also taken to observe the texture of polished surfaces.

XPS

Polished surfaces were analyzed using an X-ray photoelectron spectrometer equipped with monochromated Al K α excitation source (Quantum 2000, ULVAC-PHI, Chigasaki, Japan). Narrow survey spectra were acquired for Si 2p, C 1s, Ti 2p, and Cr 2p.

Since electrostatic surface charging leads to unexpected shift of detected peaks, a neutralization gun was in operation during analysis. C 1s spectra from the outermost surface had a peak at 284.8 eV, which was in accordance with the data of C-H or C-C bond available in published literature²⁸⁾. Hence, non-occurrence of peak shift was confirmed.

RESULTS

Surface texture

Irrespective of polishing pressure, colloidal silica suspension created a smooth mirror-like surface free from scratches (Figs. 1a and 1b).

Chromic oxide slurry under low pressure yielded a slightly undulate surface, although almost free from scratches (Fig. 1c). In contrast, high pressure led to a very uneven surface with numerous scratches (Fig. 1d).

Surface composition at EPMA level

Element analyses were made on the same areas

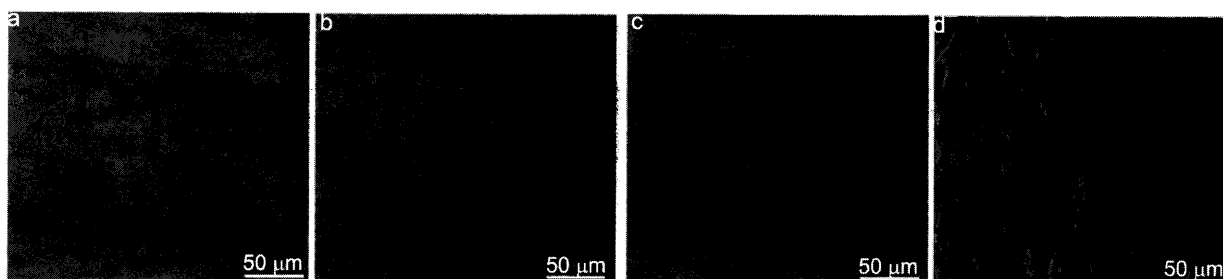


Fig. 1 SE images of polished titanium surfaces.

- a: colloidal silica suspension under low pressure;
- b: colloidal silica suspension under high pressure;
- c: chromic oxide slurry under low pressure;
- d: chromic oxide slurry under high pressure.

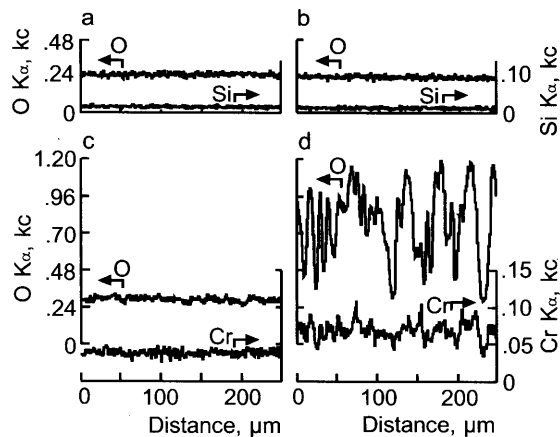


Fig. 2 Si K_{α} , Cr K_{α} , and O K_{α} intensity variations depicted along the horizontal midline of the same areas shown in Fig. 1.

- a: colloidal silica suspension under low pressure;
 b: colloidal silica suspension under high pressure;
 c: chromic oxide slurry under low pressure;
 d: chromic oxide slurry under high pressure.

shown in Fig. 1. Distributions of Si K_{α} , Cr K_{α} , and O K_{α} intensities were depicted as line profiles along the horizontal midline on the respective SE images. Concerning colloidal silica suspension, Si K_{α} intensity showed a uniform distribution at a background level, regardless of polishing pressure (Figs. 2a and 2b). O K_{α} intensity also showed a uniform distribution at the lowest level (approximately 240 counts).

When polished with chromic oxide slurry under low pressure, the surface showed slightly uneven distributions of Cr K_{α} and O K_{α} intensities. It was noted that O K_{α} intensity level rose to approximately 280 counts (Fig. 2c). When polishing pressure was high, the intensities of Cr K_{α} and O K_{α} rose high and distributed non-uniformly (Fig. 2d). In particular, it was noted that O K_{α} intensity varied widely (250 to 1200 counts). A certain correspondence between Cr K_{α} and O K_{α} intensity distributions seemed to exist, but no exact correlation was found.

Surface composition at XPS level

Si 2p, C 1s, and Ti 2p spectra were acquired at three points arbitrarily chosen on surface that was polished with colloidal silica suspension under low pressure (Fig. 3). The size of analysis point was $100\mu\text{m}$ in diameter, take-off angle was 45° , and pass energy was 58.70 eV. The intensity of Ti 2p peak from the outermost surface varied depending on the degree of carbon contamination (C 1s). A higher Si 2p peak, although absolutely low in binding energy, occurred at points where the contamination was slighter.

Cr 2p spectrum was acquired from surface polished with chromic oxide slurry under high pressure

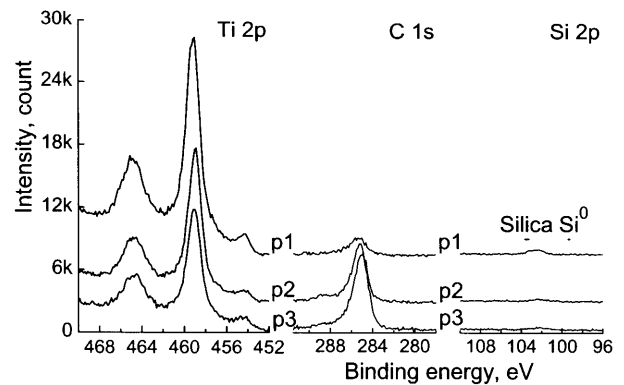


Fig. 3 Ti 2p, C 1s, and Si 2p spectra from titanium surface polished with colloidal silica suspension under low pressure, where p1, p2, and p3 mean arbitrarily chosen analysis points ($100\mu\text{m}$ in diameter).

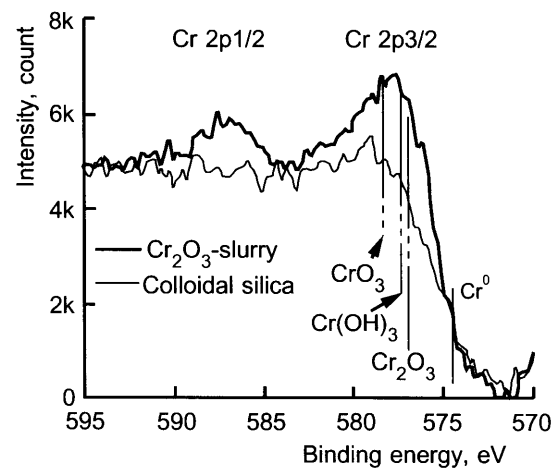


Fig. 4 Cr 2p spectrum from titanium surface polished with chromic oxide slurry under high pressure. The analyzed area was $1500 \times 500\mu\text{m}^2$.

(Fig. 4). In this analysis, the analyzed area was $1500 \times 500\mu\text{m}^2$, take-off angle was 90° , and pass energy was 117.4 eV. For reference, colloidal silica-polished surface was also analyzed in the same binding energy range. Comparison of both spectra indicated the presence of chromium-containing species in the polished surface.

DISCUSSION

Surface texture

In the present study, surface roughness was qualitatively evaluated with the naked eye and SE images. Regardless of polishing pressure, colloidal silica suspension successfully created a mirror-like surface free from scratches (Figs. 1a and 1b). In contrast, chromic oxide slurry under high pressure yielded a very uneven surface with numerous scratches (Fig. 1d). Generally, it is known that abrasive particle size is

an important factor that influences surface finishing²⁹⁾. The particle size of chromic oxide ($0.5\ \mu\text{m}$) was much larger than that of colloidal silica ($0.04\ \mu\text{m}$) (Table 1).

Hardness of abrasive material might also influence the texture of polished surface. Nevertheless, chromic oxide slurry under low pressure created a surface almost free from scratches, despite slight undulation. This suggested that polishing pressure was another important factor that influenced surface finishing.

Surface composition at EPMA level

Abrasive materials, such as $\text{SiC}^{22)}$, $\text{Al}_2\text{O}_3^{24,26)}$, and $\text{Fe}_2\text{O}_3^{25)}$, have already been reported to alter the surface composition of polished titanium. Having mechanically destroyed the protective oxide film, the abrasive material comes into direct contact with native titanium that is inherently reactive with most elements. As a result, certain reaction products are left in the oxide film that is regenerated immediately after film destruction.

Contrary to the above hypothesis, colloidal silica-polished surface was chemically clean at EPMA level (below EPMA's detection limit), even when polishing pressure was high (Figs. 2a and 2b). The colloidal silica suspension contained a colloid stabilizing agent, and its pH was 9.8. Even if silica reacted with titanium, the agent and/or the alkalinity might play a role in removing the surface reaction products.

Small variations of Cr $K\alpha$ suggested the presence of chromium in surface polished with chromic oxide slurry under low pressure (Fig. 2c). When polishing pressure was high, chromium concentration was increased with distinct positional variations (Fig. 2d). Correspondingly, oxygen concentration was noticeably varied, and its maximum reached the highest level. However, no exact correlation was found between both distributions. This might be partly caused by surface roughness: the directions normal to depression slopes were different from point to point with respect to the location of each element detector.

Surface composition at XPS level

EPMA detected chromium but not silicon in the polished surfaces. Previous EPMA and XPS investigations^{24,26)} showed that the chemical bond state of aluminum present in polished surface was entirely different from that of Al^{3+} in $\alpha\text{-Al}_2\text{O}_3$. This was probably because the polishing material reacted with titanium, and reaction products such as $\text{Ti}_x\text{Al}_y\text{O}_z$ and $\text{Ti}_x\text{Al}_y(\text{OH})_z \cdot n\text{H}_2\text{O}$ were left in the regenerated oxide film. Polishing process using ferric oxide slurry²⁵⁾ caused a similar effect. Peak shifts of Fe $L_{\alpha 1}$ and Fe $2p_{3/2}$ indicated that iron originating from the polishing material was changed into Fe^{2+} in the outer surface, while into a metallic state in the inner surface.

This finding denied the possibility that abrasive particles were mechanically embedded within titanium surface during polishing.

Based on this background, XPS was conducted to investigate whether silicon-containing species were present on the outermost surface and to determine the chemical composition of chromium-containing species. The obtained data were compared with the data of Si 2p and Cr 2p available in published literature^{31,32)}.

A small amount of silicon was present on the outermost surface (Fig. 3). Si 2p peak was located at a lower binding energy side than the peaks of various silicas. Chromium may exist as ions with different valences (Fig. 4). OH^- has been reported to be present at the outermost surface layer of oxide film on titanium³³⁾. Accordingly, a hydroxide such as $\text{Cr}(\text{OH})_3$ may also be present at the outermost surface. Although it was difficult to exactly identify these species, XPS results suggested that reactions of titanium with the abrasive material were responsible for the alteration of surface composition.

O $K\alpha$ signal in EPMA came from surface oxides and solute oxygen in the titanium substrate. Therefore, the remarkably increased amount of O $K\alpha$ (Fig. 2d) probably resulted from the increase of oxide film thickness or the extension of oxide-to-metal transition zone^{26,30)}. Pertaining to this aspect, a more detailed discussion will soon be given in another work. Nonetheless, it is worth noting again that embedment of abrasive particles within surface could not be a primary factor for the increase of oxygen concentration.

CONCLUSION

Irrespective of polishing pressure, colloidal silica suspension successfully created a mirror-like surface that was chemically clean at EPMA level. However, XPS detected a small amount of silicon on the outermost surface. Chromic oxide slurry under low pressure yielded a slightly undulate surface with small positional variations of chromium, and the level of oxygen concentration was also slightly raised. On the other hand, chromic oxide slurry under high pressure yielded a very uneven surface with numerous scratches. The EPMA and XPS results suggested the presence of chromium-containing species in the polished surface, which might include hydroxides as well as oxides. In addition, the level of oxygen concentration was noticeably raised, which probably resulted from the increase of surface oxide film thickness or the extension of oxide-to-metal transition zone. In conclusion, colloidal silica suspension was an effective agent for efficient mirror-finishing of titanium surface. This could be attributed to the ultra-fine abrasive particles and colloid stabilizing agent that were added to the suspension.

REFERENCES

- 1) Takahashi M, Kikuchi M, Takada Y, Okuno O, Okabe T. Corrosion behavior and microstructures of experimental Ti-Au alloys. *Dent Mater J* 2004; 23: 109-116.
- 2) Takemoto S, Hattori M, Yoshinari M, Kawada E, Asami K, Oda Y. Corrosion behavior and surface characterization of Ti-20Cr alloy in a solution containing fluoride. *Dent Mater J* 2004; 23: 379-386.
- 3) Nakai A. Study of resin-bonded calcia investment. Part 2: Effect of titanium content on the dimensional change of the investment. *Dent Mater J* 2002; 21: 191-199.
- 4) Meng Y, Nakai A, Goto S, Ogura H. Study of resin-bonded calcia investment. Part 3: Hardness of titanium castings. *Dent Mater J* 2004; 23: 46-52.
- 5) Takahashi J, Kitahara K, Kubo F. Phosphate-bonded ZrSiO₄ investments added with ZrC and ZrN for casting titanium. *Dent Mater J* 2004; 23: 314-320.
- 6) Yan M, Takahashi H, Nishimura F. Dimensional accuracy and surface property of titanium casting using gypsum-bonded alumina investment. *Dent Mater J* 2004; 23: 539-544.
- 7) Sato H, Komatsu M, Miller B, Shimizu H, Fujii H, Okabe T. Mold filling and microhardness of 1% Fe titanium alloys. *Dent Mater J* 2004; 23: 211-217.
- 8) Baltag I, Watanabe K, Miyakawa O. Internal porosity of cast titanium removable partial dentures – Influence of sprue direction and diameter on porosity in simplified circumferential clasps. *Dent Mater* 2005; 21: 530-537.
- 9) Keanini RG, Watanabe K, Okabe T. Theoretical model of the two-chamber pressure casting process. *Metall & Mater Trans B* 2005; 36B: 283-292.
- 10) Fujioka S, Kakimoto K, Inoue T, Okazaki J, Komasa Y. Metallurgical effects on titanium by laser welding on dental stone. *Dent Mater J* 2003; 22: 581-591.
- 11) Iwasaki K, Ohkawa S, Rosca ID, Uo M, Tsukasa Akasaka T, Watari F. Distortion of laser welded titanium plates. *Dent Mater J* 2004; 23: 593-599.
- 12) Ban S, Kadokawa A, Kanie T, Arikawa H, Fujii K, Tanaka T. Bonding strength and durability of alkaline-treated titanium to veneering resin. *Dent Mater J* 2004; 23: 424-428.
- 13) Kibayashi H, Teraoka F, Fujimoto S, Nakagawa M, Takahashi J. Surface modification of pure titanium by plasma exposure and its bonding to resin. *Dent Mater J* 2005; 24: 53-58.
- 14) Miyakawa O, Watanabe K, Okawa S, Nakano S, Shiokawa N, Kobayashi M, Tamura H. Grinding of titanium. Part 1: Commercial and experimental wheels made of silicon carbide abrasives. *J J Dent Mater* 1990; 9: 30-41.
- 15) Miyakawa O, Watanabe K, Okawa S, Nakano S, Shiokawa N, Kobayashi M, Tamura H. Grinding of titanium. Part 2: Commercial vitrified wheels made of alumina abrasives. *J J Dent Mater* 1990; 9: 42-52.
- 16) Hotta Y, Miyazaki T, Fujiwara T, Tomita S, Shinya A, Sugai Y, Ogura H. Durability of tungsten carbide burs for the fabrication of titanium crowns using dental CAD/CAM. *Dent Mater J* 2004; 23: 190-196.
- 17) ADA council on scientific affairs. Titanium application in dentistry. *JADA* 2003; 134: 347-349.
- 18) Kikuchi M, Takahashi M, Okabe T, Okuno O. Grindability of dental cast Ti-Ag and Ti-Cu alloys. *Dent Mater J* 2003; 22: 191-205.
- 19) Kikuchi M, Takahashi M, Okuno O. Mechanical properties and grindability of dental cast Ti-Nb alloys. *Dent Mater J* 2003; 22: 328-342.
- 20) Kikuchi M, Okuno O. Machinability evaluation of titanium alloys. *Dent Mater J* 2004; 23: 37-45.
- 21) Takahashi M, Kikuchi M, Okuno O. Mechanical properties and grindability of experimental Ti-Au alloys. *Dent Mater J* 2004; 23: 203-210.
- 22) Miyakawa O, Watanabe K, Okawa S, Kanatani M, Nakano S, Kobayashi M. Surface contamination of titanium by abrading treatment. *Dent Mater J* 1996; 15: 11-21.
- 23) Miyakawa O. Reactivity of titanium with abrasive materials and its polishing. *J Jpn Prosthodont Soc* 1998; 42: 540-546.
- 24) Miyakawa O, Okawa S, Kobayashi M, Uematsu K. Surface contamination of titanium by abrading treatment. *Dentistry in Japan* 1998; 34: 90-96.
- 25) Akhter R, Okawa S, Nakano S, Kobayashi M, Miyakawa O. Surface composition and structure of titanium polished with aqueous slurry of ferric oxide. *Dent Mater J* 2000; 19: 10-21.
- 26) Okawa S, Hossain A, Kanatani M, Watanabe K, Miyakawa O. Surface properties of electrochemically buffed titanium casting. *Dent Mater J* 2004; 23: 504-511.
- 27) Miyakawa O, Watanabe K, Okawa S, Nakano S, Kobayashi M, Shiokawa N. Layered structure of cast titanium surface. *Dent Mater J* 1989; 8: 175-185.
- 28) Moulder JF, Stickle WF, Sobol PE, Bomben KD. Handbook of X-ray photoelectron spectroscopy, Physical Electronics Inc, Minnesota, 1995, pp.216.
- 29) Williams D. Biocompatibility of implants materials, Sector Publishing Limited, London, 1976, pp.38.
- 30) Brunette DM, Tengvall P, Textor M, Thomsen P. Titanium in medicine, Springer, Berlin, 2001, pp.154-162.
- 31) Moulder JF, Stickle WF, Sobol PE, Bomben KD. Handbook of X-ray photoelectron spectroscopy, Physical Electronics Inc, Minnesota, 1995, pp.56-57, 238.
- 32) Moulder JF, Stickle WF, Sobol PE, Bomben KD. Handbook of X-ray photoelectron spectroscopy, Physical Electronics Inc, Minnesota, 1995, pp.76-77, 219.
- 33) Brunette DM, Tengvall P, Textor M, Thomsen P. Titanium in medicine, Springer, Berlin, 2001, pp.178-185.